Ammonium Distribution in the Labrador Sea and Adjacent Waters

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by

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ABSTRACT

Harrison, W.G.. 2013. Ammonium Distribution in the Labrador Sea and Adjacent Waters. Can. Tech. Rep. Hydrogr. Ocean. Sci. 280: v + 34 pp.

Water samples from 133 stations, collected from nine missions (1999-2012) of the Labrador Sea Monitoring Program occupied between May and July, were analyzed for ammonium (NH_4). Depth profiles showed shallow (median = 50 m) subsurface NH_4 maxima (up to 4 μM) at 64% of the stations. The subsurface maxima were deeper than the chlorophyll *a* maxima (median = 20 m) and at or below the depths of the euphotic zone (median = 45 m). Subsurface NH_4 maxima were seen in all regions and months but were most prevalent in the east, off the coast of Greenland, and in July. The more pronounced NH_4 maxima in the eastern Labrador Sea were linked to early and large spring phytoplankton blooms and associated with the inflow of North Atlantic and Greenland Shelf waters. Elevated NH_4 concentrations extending to the seafloor also suggested involvement of the benthos on the shallow Greenland Shelf. On average, NH_4 represented a relatively small fraction of the inorganic-N inventory of the upper water column (median = 6-8%) but exceeded 30% at stations where subsurface maxima were large. NH_4 concentrations in deeper Labrador Sea waters (200-3600 m) were low (median = 0.24-0.31 μM) yet variable with depth. The vertical structure, concentration and net accumulation rate of NH_4 over time in the subsurface maximum in the Labrador Sea were consistent with results from other high latitude field studies and from ocean models for the north Atlantic and Pacific where NH_4 dynamics in the upper ocean are governed largely by the balance of uptake (principally by phytoplankton) and regeneration by heterotrophs (zooplankton and bacteria).

RÉSUMÉ

Harrison, W.G. 2013. Distribution de l'ammonium de la mer du Labrador et des mers adjacentes. Can. Tech. Rep. Hydrogr. Ocean. Sci. 280: v + 34 p.

Des échantillons d'eau provenant de 133 stations, recueillis dans le cadre de neuf missions (de 1999 à 2012) du Programme de monitorage de la mer du Labrador et effectués entre mai et juillet, ont été analysés pour déceler la présence d'ammonium (NH_4). Les profils de profondeur ont indiqué des valeurs maximales de subsurface (jusqu'à 4 □M) de NH_4 en eau peu profonde (médiane = 50 m) à 64 % des stations. Les valeurs maximales de subsurface étaient dans des eaux plus profondes que les valeurs maximales de la chlorophylle *a* (médiane = 20 m) et dans des eaux aussi profondes ou plus profondes que la zone euphotique (médiane = 45 m). Les valeurs maximales de subsurface de NH_4 ont été observées dans toutes les régions et à tous les mois, mais elles étaient plus fréquentes à l'Est, au large du Groenland, et au mois de juillet. Les valeurs maximales de NH_4 les plus prononcées à l'est de la mer du Labrador étaient liées au début de la prolifération printanière du phytoplancton et associées aux apports d'eau de l'Atlantique Nord et du plateau du Groenland. Des concentrations élevées de NH_4 s'étendant au fond marin ont également indiqué une implication possible du benthos dans le plateau du

Groenland peu profond. En moyenne, le NH_4 représentait une fraction relativement faible de l'inventaire d'azote inorganique de la partie supérieure de la colonne d'eau (médiane = 6 à 8 %) mais il était supérieur à 30 % aux stations où les valeurs maximales de subsurface étaient importantes. Les concentrations de NH_4 dans les eaux plus profondes de la mer du Labrador (200 à 3 600 m) étaient faibles (médiane = 0,24 à 0,31 □M), mais variaient selon la profondeur. La structure verticale, la concentration et le taux d'accumulation nette du NH_4 au fil du temps dans la valeur maximale de subsurface de la mer du Labrador étaient cohérents avec les résultats provenant d'autres études sur le terrain dans les eaux des hautes latitudes et des modèles océaniques de l'Atlantique Nord et du Pacifique où la dynamique du NH_4 dans la couche supérieure de l'océan est régie par l'équilibre entre l'absorption (principalement par le phytoplancton) et la régénération par les hétérotrophes (zooplancton et bactéries).

1. INTRODUCTION

Ammonium is a highly reactive molecule in seawater and important component of the inorganic nitrogen pool of the surface ocean. It is an intermediary in the breakdown of organic matter by marine heterotrophs, has a short turnover time (hours to days) and plays a critical role in the nutrition of both phytoplankton and bacteria and as a structural component of biomass (protein) or as an energy source when oxidized to the more chemically stable nitrate. Typically, ammonium (NH_4) concentrations are low (tenths of a μM) to undetectable in near surface ocean waters. However, it is not uncommon to see elevated concentrations (up to several μM) that peak at depths below the surface mixed layer (e.g. Saino et al. 1983). The vertical structure of NH_4 is thought to be governed largely by biological processes and result from a balance between uptake, largely by autotrophs (phytoplankton), and regeneration by heterotrophs (zooplankton, microbes) also vertically structured in the water column (Jamart et al. 1977, 1979).

Although NH_4 has not been designated a core nutrient variable in the suite of chemical measurements made by the 20-year Labrador Sea Monitoring Program (Greenan et al, 2010), intermittent measurements made since 1999 provide sufficient observations to evaluate some aspects of the spatial and temporal distribution of this important constituent of the ocean nitrogen cycle. Among the more interesting features discovered in the Labrador Sea analysis is the occurrence of a well-defined subsurface NH_4 maximum layer, observed during almost all missions and geographic locations where vertical profiles of NH_4 were made.

This report provides a preliminary description of the spatial distribution and temporal variability of ammonium in the Labrador Sea area. It is not a comprehensive analysis of the processes that govern regional NH_4 dynamics but a comparison of observations with results from other studies and it opens some discussion on hypotheses that help explain ammonium distribution in oceanic waters and, more specifically, the formation of the subsurface ammonium maximum. Thus, this account should provide some of the background information useful for a more thorough analysis of NH_4 in the region and its biogeochemical significance.

2. METHODS

a. Sampling

Primary sampling was done along the "L3 Line", also referred to as the "AR7/W" WOCE repeat hydrographic section (e.g. Yashayaev 2007). Discrete samples were collected at 30-31 nominal stations from the Labrador to Greenland coasts (Figure 1). Water samples were collected using a CTD-rosette system outfitted with 24 10L PVC sampling bottles. Water samples were collected from 11 depths (shallow stations <200 m) to 24 depths (deep stations to >3600 m depth) along the line. Additional stations along other lines or in transit to and from L3 were sampled in some years. The L3 line has been occupied at least once annually since 1994, however, ammonium measurements did not begin until 1999, ran for 6 years, and then began again in 2010 (Table 1). During the early missions (1999-2004) ammonium samples were generally collected in the upper 200 m (8-10 depths); there were a few full-depth profiles generated in the central Labrador Basin during those years. Starting in 2010, full-depth

ammonium profiles were generated for all stations along the L3 Line. Occupation of stations in the Labrador Sea area ranged from 6-10 days (avg = 8 d) and started as early as the second week in May to as late as the third week in July (Figure 2).

b. Analytical

Ammonium (NH_4) was measured colourometrically using manual methods (Solórzano 1969) on freshly collected samples during the early missions (1999-2004) and fluorometrically (Kerouel et al. 1997) by auto-analyzer during the latter missions (2010-2012). The methods give comparable results with replicate precision of 5-10% and detection limits, based on 3X std dev of blanks, of 0.05-0.10 μM (= mmol m^{-3}). Operationally, however, detection limits may be as much as 2-3X higher based on measurements in deep waters (See Results section). Nitrate (NO_3) was measured on all missions using standard auto-analyzer methods (Technicon II). Nitrite (NO_2) was measured separately only in 2011 and 2012. Chlorophyll *a* (CHL) was measured fluorometrically (Holm-Hansen et al. 1965). Vertical profiles of physical properties of the water column (e.g. temperature, salinity, irradiance) and fluorescence were measured continuously using an instrumented CTD-rosette system (Seabird SBE 25, LICOR, Chelsea Instruments). All data described in this report have been archived in BIO's Climate or BIOCHEM databases (http://www.dfo-mpo.gc.ca/science/data-donnees/index-eng.html).

3. RESULTS

NH_4 samples were collected at 133 stations over nine Labrador Sea missions from 1999-2012, 10 stations were in transit and 123 in the Labrador Sea area (Figure 1, Table 1). Thirty-nine (39) of the stations were on the broad Labrador Shelf/Slope, 68 in the central Labrador basin and 16 on the narrow Greenland shelf/slope. Of the 123 stations sampled in the Labrador Sea area, 79 stations (64%) exhibited subsurface NH_4 maxima (Table 1). Stations exhibiting subsurface maxima varied by cruise and time of year of sampling with the percentage of subsurface maxima higher during the missions occurring later in the year (Figure 3).

a. Vertical Profiles

NH_4 profiles were grouped into six broad categories: Labrador shelf/slope stations where subsurface NH_4 maxima were observed or absent, central Labrador basin stations where subsurface NH_4 maxima were observed or absent, central Labrador basin stations where broad subsurface maxima were observed and Greenland shelf/slope stations where elevated subsurface NH4 concentrations extended to the sea floor.

Profiles with no discernible subsurface NH_4 maxima were prevalent in the Labrador shelf/slope region for most of the years sampled (Figure 4). Typically, these stations were in fairly shallow waters well onto the shelf, with high surface chlorophyll *a* levels and a distinct cold intermediate layer (CIL) with coldest temperatures at ~ 50 m depth. Some shelf/slope stations, however, exhibited modest subsurface NH_4 maxima (Figure 5); the largest maxima were observed during the summer missions particular in 2003 (see Figure 2). NH_4 peaks were generally found below the chlorophyll *a* maximum and on the upper shoulder of the CIL. Of the 39 profiles measured on the Labrador coast, 15 (38%) exhibited subsurface NH_4 maxima.

There were also stations in the central Labrador basin with no apparent subsurface NH_4 maxima (Figure 6) but stations with subsurface maxima were more common and occurred more

frequently than on the coast (Figure 7). Relatively sharp (60-70 m thickness), subsurface peaks were typically large (>2 μM), compared with surface concentrations (<0.5 μM), located meters below the subsurface chlorophyll *a* maxima and at the base of the thermocline. Broader subsurface peaks (100-200 m thickness) were also observed in the central basin, most often seen on the eastern side (Figure 8). Of the 68 profiles measured in the central Labrador basin, 48 (71%) exhibited subsurface NH_4 maxima.

Elevated subsurface NH_4 concentrations were also seen along the narrow Greenland shelf/slope region, however, subsurface peaks were not seen but concentrations were uniformly high or increased to the sea floor (Figure 9). NH_4 concentrations began to increase at the base of the chlorophyll *a* maximum and at the near-surface temperature minimum. There was no exception to this pattern and it was seen repeatedly during all missions, i.e. all 16 profiles (100%) measured during this study. As mentioned earlier, overall, 79 of the 123 profiles (64%) measured in this study exhibited elevated subsurface NH_4 concentrations (Table 1).

Over all missions/stations, the depth of the subsurface NH4 maximum (median = 50 m) was significantly deeper than that of the chlorophyll *a* maximum (median = 20 m) and at or slightly deeper than the euphotic depth, 1% light level (median = 45 m) (Figure 10).

Full-depth NH_4 profiles showed relatively uniform and low concentrations below >200 m (Figure 11) although the range of values at any particular depth generally equaled or exceeded the mean. Median concentrations at depth were 0.24 μM (90 %tile = 0.16-0.37 μM), 0.24 μM (90 %tile = 0.15-0.39 μM) and 0.31 μM (90 %tile = 0.23-0.45 μM) in 2010, 2011 and 2012, respectively. Two deep profiles were also generated during the earlier, 2001, mission (not shown); concentration were slightly lower than in 2010-2012; median concentration = 0.09 μM (90 %tile = 0.05-0.30 μM). The high dispersion of data in these deep profiles make interpretation of the results difficult.

In 2011 and 2012, NO_2 analyses were added. As in the case of NH_4, subsurface NO_2 maxima in the upper water column were observed at a number of stations (Figure 12) but less frequently than NH_4, i.e. 27% of the profiles exhibited subsurface NO_2 peaks, whereas 58% exhibited subsurface NH_4 peaks. Subsurface NO_2 peaks were also deeper than NH_4 peaks: median depth was 87 m for NO_2 compared to 52 m for NH_4, a difference of 35 m. NO_2 concentrations were relatively uniform with depth below ~750 m; median levels were 0.09 μM in 2011 and 2012 (90 %tile = 0.08-0.12 μM).

b. Spatial Distribution

In addition to recurring patterns in the vertical structure of NH_4, patterns were also seen in geographic distribution. For example, over all mission, the magnitude of the subsurface NH_4 maximum tended to increase from west to east along the L3 line (Figure 13), similar to temperature differences between the surface and NH_4 maximum. Depths of the subsurface maxima, on the other hand, showed no west–to-east trend. Surface NH_4 concentrations were geographically variable and decreased slightly overall from May to July; monthly median values = 0.30, 0.29 and 0.26 μM (Figure 14). Concentrations at the NH_4 maximum were considerably higher than surface levels and increased overall from May to July; median concentrations = 0.63, 0.89 and 1.12 μM (Figure 15). Subsurface concentrations were somewhat higher off the coast of Greenland in May and June but more geographically uniform in July. A similar geographic and temporal pattern was seen in the difference in NH_4 concentrations between the surface and depth

of maximum (Figure 16). Overall, no geographic or temporal pattern was seen in the depth of the NH_4 maximum, median depth = 50 m (Figure 17).

Inventories of NH_4 (integrals in the upper 100 m) were compared with NO_3 and NO_2 inventories to determine if the occurrence of subsurface NH_4 maxima resulted in a significant contribution to the inorganic-N pool in the upper water column. Median levels of NH_4 during May missions was 43 mmol m^{-2} compared to 707 mmol m^{-2} and 19 mmol m^{-2} for NO_3 and NO_2, respectively. In June, inventories were 52, 668 and 15 mmol m^{-2} for NH_4, NO_3 and NO_2 and in July NH_4 levels were 63 mmol m^{-2} and NO_3 were 737 mmol m^{-2}; NO_2 was not measured in July. On average, NH_4 represented only 6-8% of the total inorganic-N in the upper water column, although at some stations, the percentage was as high as 36%; highest percentages were seen in the eastern Labrador Sea in May and June but were more widespread in July (Figure 18).

c. Water Mass

Sparse sampling during the early missions (1999-2004) provided only a coarse representation of the spatial distribution of NH_4 in the Labrador Sea. However, more intense sampling (all depths/stations along the L3 line), starting with the 2010 mission, provided the data density required to construct a much more detailed picture of the upper water column distribution of NH_4 and its relationship to regional water masses. As discussed earlier, NH_4 concentrations below 200 m were low (<0.5 μM), relatively uniform with depth and similar between years (Figure 11). In shallower waters, higher NH_4 concentrations (>0.5 μM) were typical and largely confined to the eastern basin of the Labrador Sea based on vertical sections of the L3 Line for all of the 2010-2012 missions (Figure 19). These distributional patterns suggest that water masses entering the Labrador Sea and offshore flow from the Greenland Shelf might be contributing to the higher concentrations in the eastern sector. Indeed, section plots of temperature show coherence between the distribution of NH_4 and the interaction between the warm/salty North Atlantic water (>4 °C, I. Yashayaev, pers comm) and cold/fresh Greenland Shelf waters (Figure 20), transported by the Irminger and West Greenland Currents, respectively (Yashayaev 2007). T-S property plots (Figures 21, 22) also show that the high NH_4 concentrations were most frequently associated with the eastern Labrador Basin and Greenland shelf/slope regions that are influenced by the water masses described above.

4. DISCUSSION

a. Vertical Structure

Saino et al. (1983) were among the first to describe subsurface NH_4 maxima as a common feature of the upper water column in the northern North Pacific and Bering Sea in summer. They described two types of distributions, one in which the subsurface maxima were associated with distinct water mass features and one with maxima in bottom waters associated with the seabed. The maxima in the water column were commonly found at 30-50 m in waters >100 m depth and associated with a sharp pycnocline near the bottom of the euphotic zone and below the subsurface chlorophyll *a* maximum. Coincident measurements of microbial activity indicators led to the speculation that the NH_4 maxima were of autochthonous origin and likely the product of zooplankton grazing/excretion and/or bacterial decomposition. Similar vertical NH_4 profiles have been observed in other northern sub-polar and polar waters (Owrid et al. 2000,

Woodward and Rees 2001, Martin et al. 2010) and in the southern ocean (Gordon et al. 2000, Bode 2002). Some studies have linked the offshore subsurface NH_4 maxima to water mass advection from shallow coastal waters (Eppley et al 1979, Mordy et al. 2008) but most have concluded that the feature is a product of seasonal *in situ* biological decomposition following the spring phytoplankton growth event. In general, all of these studies have noted that the subsurface NH_4 maxima is found below the chlorophyll *a* maximum, near or below the bottom of the euphotic zone and associated either with maxima in activity or distribution of heterotrophs (bacteria or zooplankton grazers) or with NH_4 production at/near the seafloor by benthic regeneration. Detailed observations of bacterial abundance in the Labrador Sea have not revealed subsurface maxima but have shown a more or less logarithmic decrease in cell counts with depth (WKW Li, pers comm). Although data on the fine-scale vertical distribution of zooplankton are not available for the Labrador Sea, measurements made further north (Herman 1983, Longhurst et al. 1984), under similar conditions in summer, indicated that secondary mesozooplankton maxima, below the chlorophyll *a* maxima, were commonly observed. Moreover, generally greater abundance of zooplankton in the eastern Labrador Sea than in the central basin or Labrador Shelf (Head et al. 2000, 2003) is also consistent with the prevalence and higher concentrations in the subsurface NH_4 maxima of the eastern Labrador Sea basin and Greenland Shelf.

Indeed, early 1-D and 2-D ecosystem models (e.g. Jamart et al. 1977, 1979) argued that a subsurface NH_4 maximum will develop below the chlorophyll *a* maximum where regenerative processes exceed uptake. More complex, coupled 3-D physical-biological modeling studies have shown that a subsurface NH_4 maximum develops following the decline of the spring bloom in the North Atlantic, 46-51 N (McGillicuddy at al. 1995a, b). Output from this model compared favourably with field data and showed subsurface NH_4 maxima developing during and peaking after the spring phytoplankton bloom; at ~45 m and below the chlorophyll *a* maximum (~25 m). Heterotrophs (microzooplankton) accounted for the development of the subsurface NH_4 maximum in this study. These results are fully consistent with the studies described above and the observations we made in the Labrador Sea.

Subsurface NO_2 maxima, also referred to as the primary nitrite maximum (PNM), were also observed in the Labrador Sea but less frequently that subsurface NH_4 maxima. Moreover, the PNM occurred deeper (by ~35 m) than the NH_4 maxima and considerably deeper (by >65 m) than the chlorophyll *a* maximum. It is generally accepted that the PMN is generated from incomplete reduction of NO_3, and subsequent excretion, by phytoplankon under low light conditions (i.e. at or near the base of the euphotic zone) or generated by the oxidation of NH_4 by microbial nitrifiers below the euphotic zone, or a combination of those processes (Lomas and Lipschultz 2006). The vertical structure of the chlorophyll *a* maximum, NH_4 maximum and PNM and temporal patterns in peak formation are considered to be a strong indication of the processes that mediate the formation of the PNM (Meeder et al. 2012, see also Mordy et al. 2010). Close proximity of the PMN and the chlorophyll *a* maximum suggests that phytoplankton excretion is the primary driver; this is most commonly observed during or immediately after the spring phytoplankton bloom. Alternatively, large vertical displacement of the corresponding peaks, often seen well after the phytoplankton growth season, suggests that nitrification dominates. Since the PNM in the Labrador Sea is consistently much deeper than the chlorophyll *a* maximum, and below the NH_4 maximum, it must be concluded that microbial nitrification is the most likely underlying process accounting for the feature, despite the fact that sampling in 2011 and 2012 were in spring and early in the phytoplankton growth cycle.

b. Temporal Trends

Long term (interannual to decadal) trends in key chemical (inorganic nutrients) and biological (phytoplankton and bacteria) properties of the Labrador Sea have been established from 20 years of observations in the region (Greenan et al. 2012). Ammonium, because of its biological reactivity, is more ephemeral in nature and major variability in residual concentrations is seen on the seasonal time scale. For that reason, it is hard to establish any long term trends in NH_4 from these observations.

On the shorter time scale, however, and following from the observational and modeling studies that have established a link between the growth cycle of phytoplankton and the development of a subsurface NH_4 maximum, the prevalence of large subsurface NH_4 maxima, especially in the eastern Labrador Sea may be tied to the timing and magnitude of annual phytoplankton bloom in that region. One of the most conspicuous features of the phytoplankton growth cycle in the Labrador Sea is the early and intense spring bloom in the shelf/slope waters off the Greenland coast (Figure 23; see also Head et al. 2000, Wu et al. 2008, Frajka-Williams and Rhines 2010, Harrison et al. 2013). During the years of the present study, the spring bloom off the Greenland coast peaked as early as late April (YD = 118) and mid-May (YD = 139) on the average. This compared to the average peak of the spring bloom occurring in early June (YD = 154) off the Labrador coast and mid to late June (YD = 172) in the central Labrador basin. In addition to an earlier bloom off the Greenland coast, its magnitude, at times >12 $\mu g\ L^{-1}$ chlorophyll *a* (CHL) and averaging 4.77 μg CHL L^{-1}, was significantly higher than the blooms off the Labrador coast (avg peak = 2.01 μg CHL L^{-1}) and the central basin (avg peak = 1.35 μg CHL L^{-1}). Recent observational and modeling studies in the Labrador Sea have confirmed this phytoplankton growth pattern and explain the early bloom off the coast of Greenland by freshwater-driven (ice melt, enhanced regional precipitation) early onset of stratification, enhanced eddy activity and off-shelf advection (Wu et al. 2008, Frajka-Williams and Rhines 2010). It therefore follows that larger (and earlier) blooms in the eastern Labrador Sea can help explain the regionally larger and more prevalent subsurface NH_4 maxima there. Off-shelf transport may also help explain the NH_4 distribution patterns seen in vertical sections along the eastern side of the L3 line in 2010-2012 as discussed previously (see Figure 19).

Although the goal of the Labrador Sea monitoring program has been to execute the annual missions at approximately the same time of year to avoid seasonal bias, various factors have contributed to a less than desirable mission timing occurring from early May to late July (see Figure 2). From the standpoint of NH_4 dynamics, however, this has provided, fortuitously, an opportunity to investigate the development of the subsurface NH_4 maximum as the biological growth season progressed. The early missions (1999-2004), alone, spanned the major periods of: rapid phytoplankton growth, peak abundance and early decline. With this in mind, a plot of the median concentration of NH_4 in the subsurface maximum by mission (and thus by day of the year) revealed a near linear increase in concentration with time (Figure 24; note the similar increase in temperature at the NH_4 maximum depth). The "net" accumulation rate of NH_4 was ~20 nM d^{-1}. During those missions the biological uptake of NH_4 was measured at selected depths within the upper water column (see Harrison et al. 2013) and ranged from ~20-40 nM d^{-1} at the depth of the subsurface NH_4 maximum. This would mean that the absolute, or "gross", NH_4 production in the subsurface maximum would range from ~40-60 nM d^{-1}. E. Head (pers comm) has indicated that mesozooplankton could be contributing as much as 10 nM d^{-1} of that flux, the balance (~75-85%) presumably being microbial in origin. This net accumulation rate

was about half of the modeled rate in the subsurface maximum in the McGillicuddy et al (1995 a,b) study of the spring phytoplankton bloom in the NW Atlantic, i.e. they calculated a "net" NH_4 accumulation rate of ~40-50 nM d^{-1}. However, temperatures at the NH_4 maximum depth (12-13 °C) were considerably higher in their study at 46-51 °N than in the Labrador Sea study at 53-61 °N (2-5 °C). The depth of the subsurface NH_4 maximum (~45 m) and its position relative to the chlorophyll *a* maximum (~25 m) in their study, on the other hand, were remarkably similar to the structure observed in the Labrador Sea where the NH_4 maximum was generally found at ~50 m and the chlorophyll *a* maximum at ~20 m.

This study has shown that the presence of a subsurface NH_4 maximum is a common feature in the Labrador Sea, as in other high latitude oceans, and that its prominence is closely linked to the biological growth cycle in the region. Because NH_4, and the subsurface maximum in specific, generally represents only a small fraction (<10 %) of the inventory of inorganic-N reserves (see Figure 18), its biogeochemical significance may lie more in its role as an indicator of the competing assimilative and regenerative processes that govern the vertical biological structure of the upper ocean rather than its contribution to regional productivity.

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The officers and crew of CCGS Hudson and scientific staff of the Ocean Sciences Division (OSD), Ecosystem Research Division (ERD) and, more recently, the Ocean and Ecosystem Sciences Division (OESD) provided invaluable support to the Labrador Sea Monitoring Program. Les Harris and Carol Anstey assisted with the collection and analysis of nutrient samples. Financial support for this work came from the Program of Energy Research and development (PERD), in the early years, and, more recently, from Fisheries and Oceans (DFO) regular operating funds for core programs. Bill Li and Phil Yeats provided helpful comments in the preparation of this report.

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TABLES

Table 1: Labrador Sea missions, 1999-2012.

Mission	Year	Dates	Year Day (avg)	NH4 profile Stns (#)	# Profiles with subsurface NH4 Max
99022	1999	01 Jul – 11 Jul	187	11	10
2000009	2000	28 May – 05 Jun	153	7	3
2001012	2001	04 Jun – 11 Jun	159	9	7
2002032	2002	02 Jul – 08 Jul	186	17	15
2003038	2003	23 Jul – 29 Jul	207	9	9
2004016	2004	20 May – 28 May	145	7	0
2010014	2010	17 May – 24 May	141	18	8
2011009	2011	11 May – 22 May	137	28	16
2012001	2012	04 Jun – 12 Jun	160	17	11
TOTAL:				123	79

FIGURES

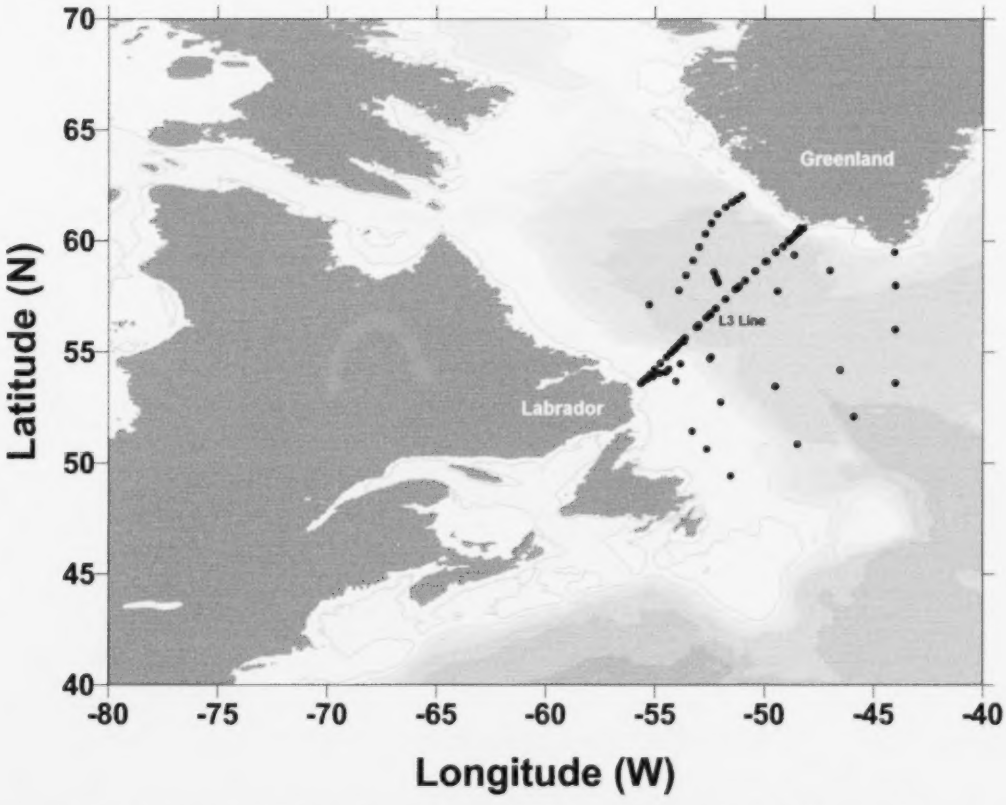

Figure 1: Labrador Sea area ammonium (NH_4) profile stations, 1999-2012.

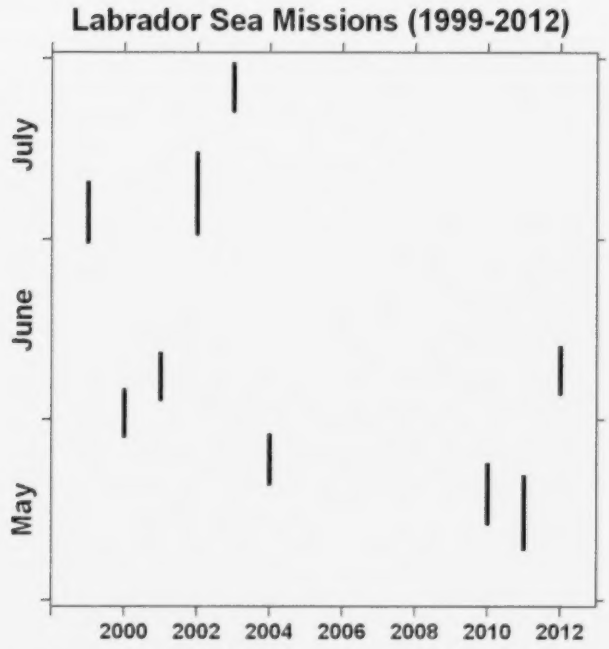

Figure 2: Mission dates/duration, 1999-2012.

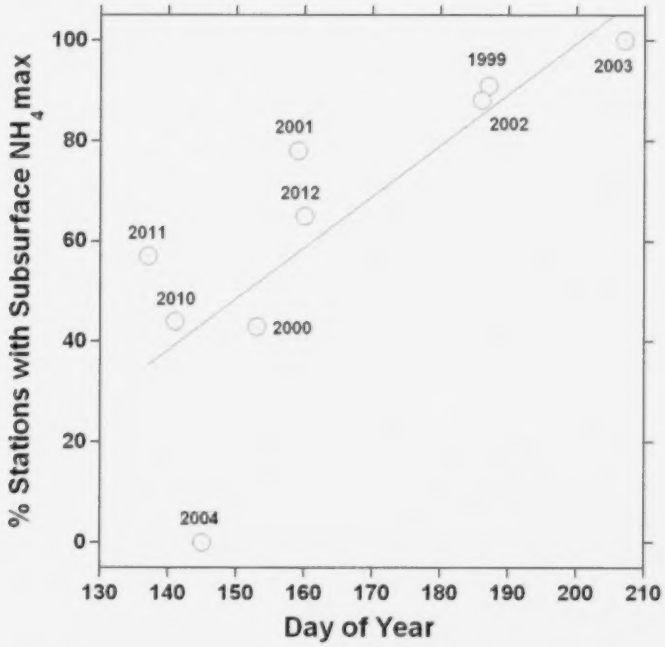

Figure 3: Percentage of stations exhibiting a subsurface NH_4 maximum. Line is least-squares linear fit.

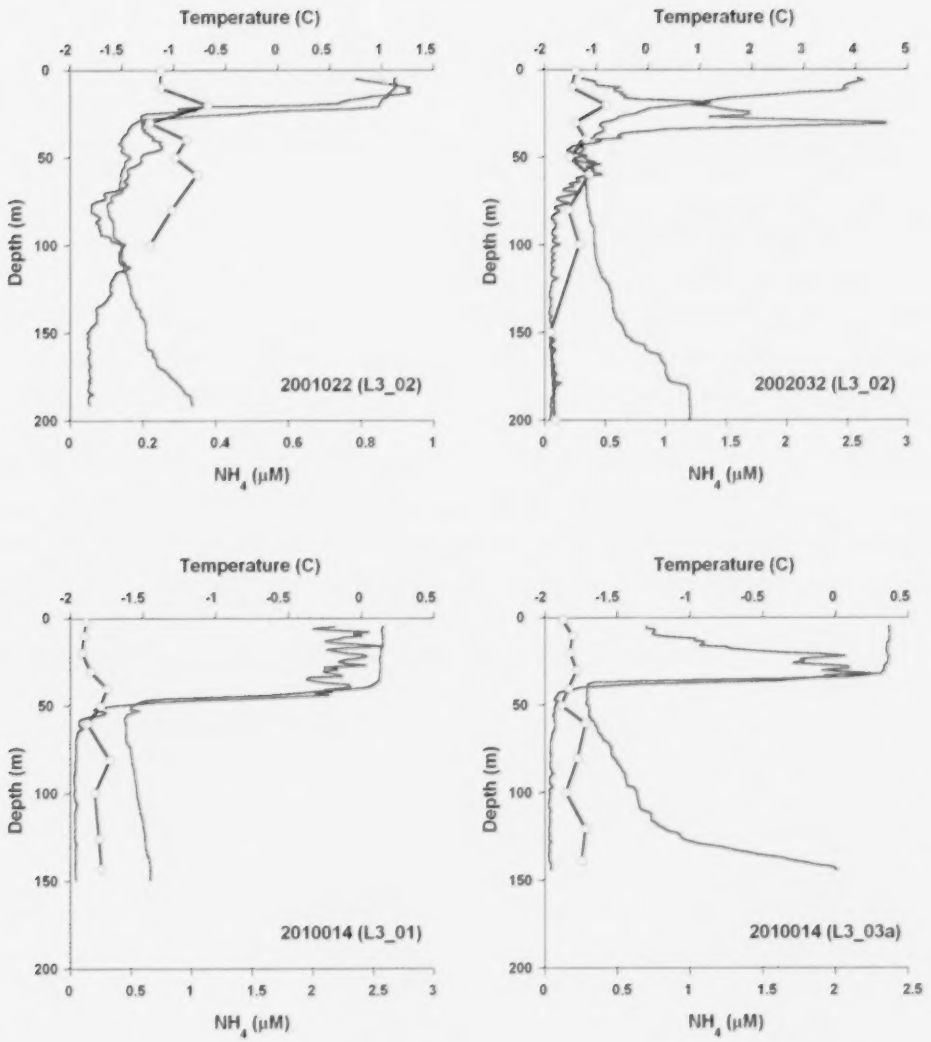

Figure 4: Vertical profiles (upper 200 m) of temperature (^{o}C, red), chlorophyll fluorescence (rel units, green) and NH_4 (μM, blue), Labrador Shelf: no subsurface NH_4 maximum.

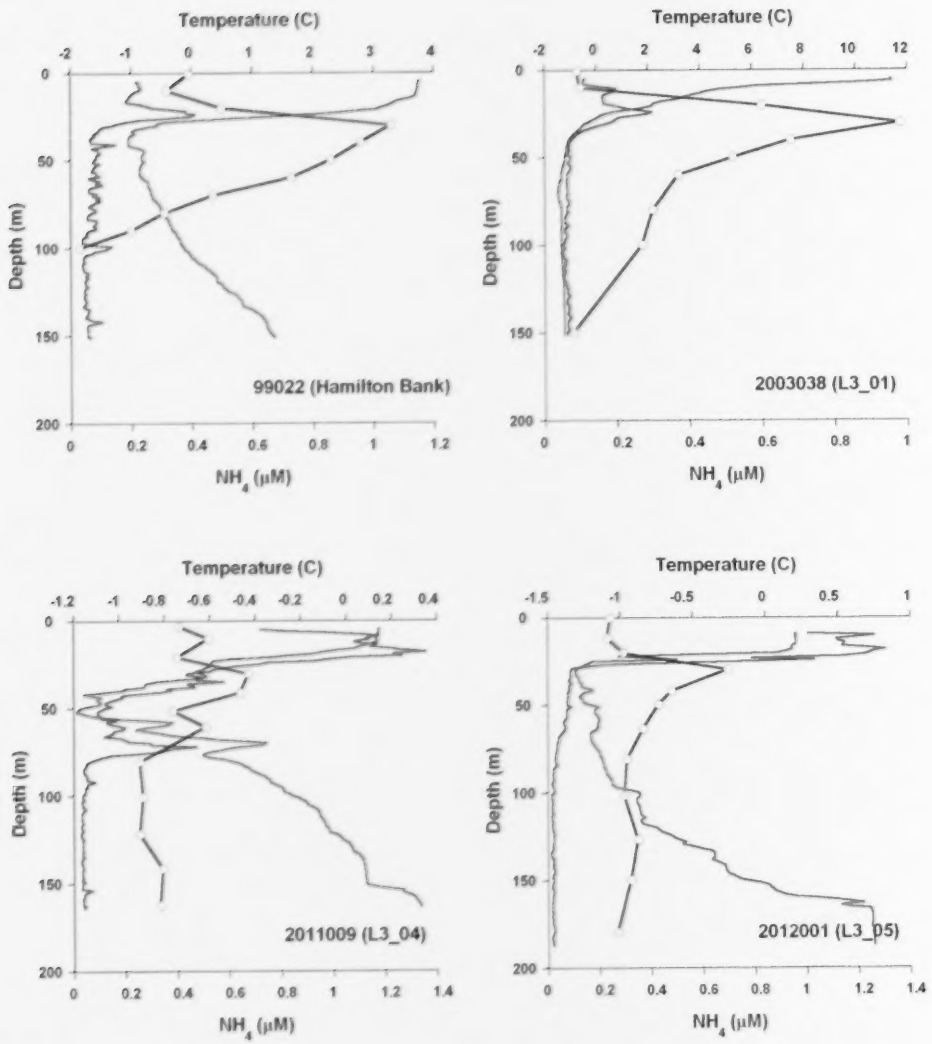

Figure 5: Vertical profiles (upper 200 m) of temperature (^{o}C, red), chlorophyll fluorescence (rel units, green) and NH_4 (µM, blue), Labrador Shelf: subsurface NH_4 maximum.

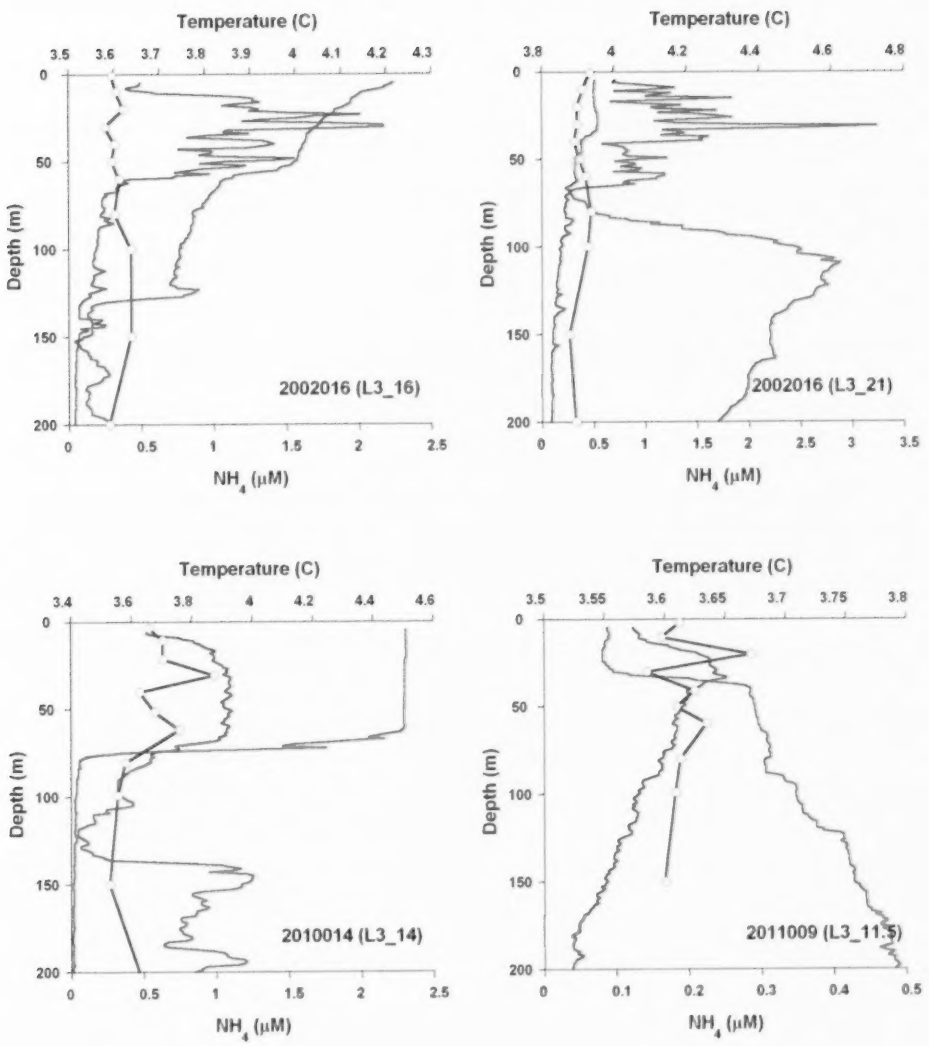

Figure 6: Vertical profiles (upper 200 m) of temperature (^{o}C, red), chlorophyll fluorescence (rel units, green) and NH_4 (µM, blue), Central Labrador Basin: no subsurface NH_4 maximum.

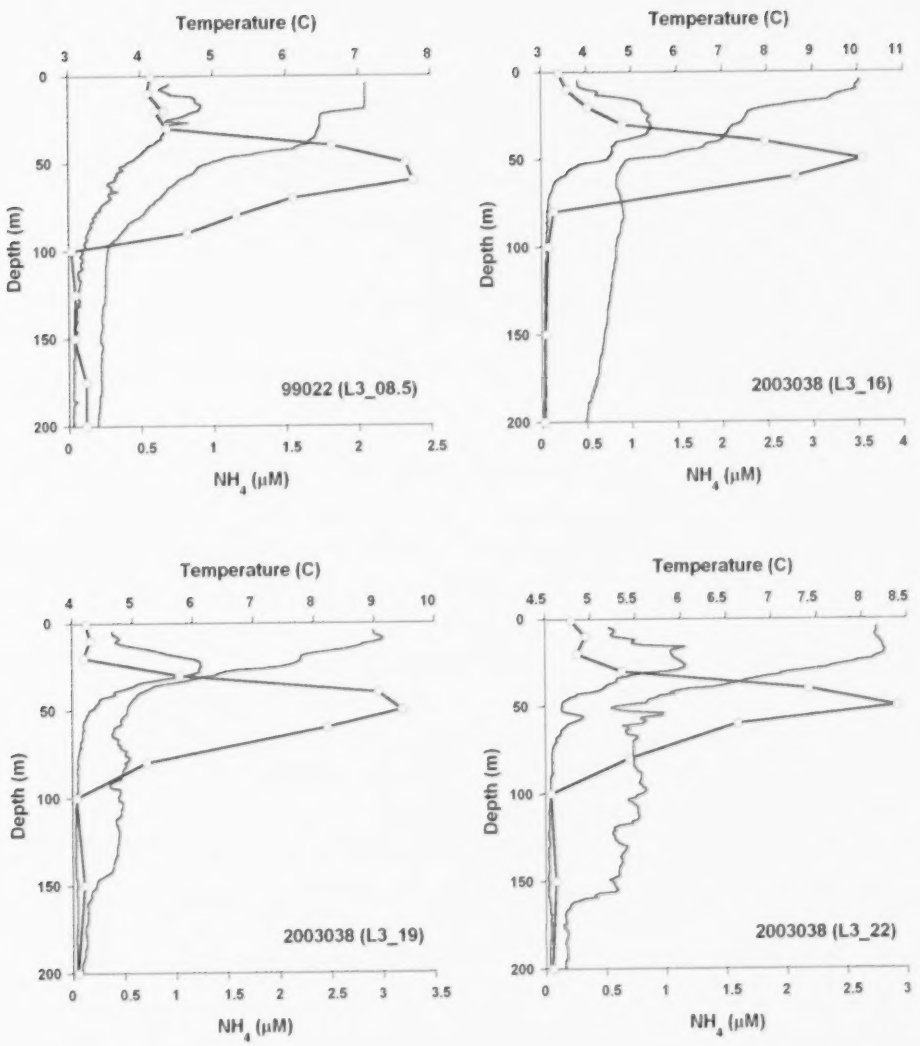

Figure 7: Vertical profiles (upper 200 m) of temperature (°C, red), chlorophyll fluorescence (rel units, green) and NH_4 (μM, blue), Central Labrador Basin: subsurface NH_4 maximum.

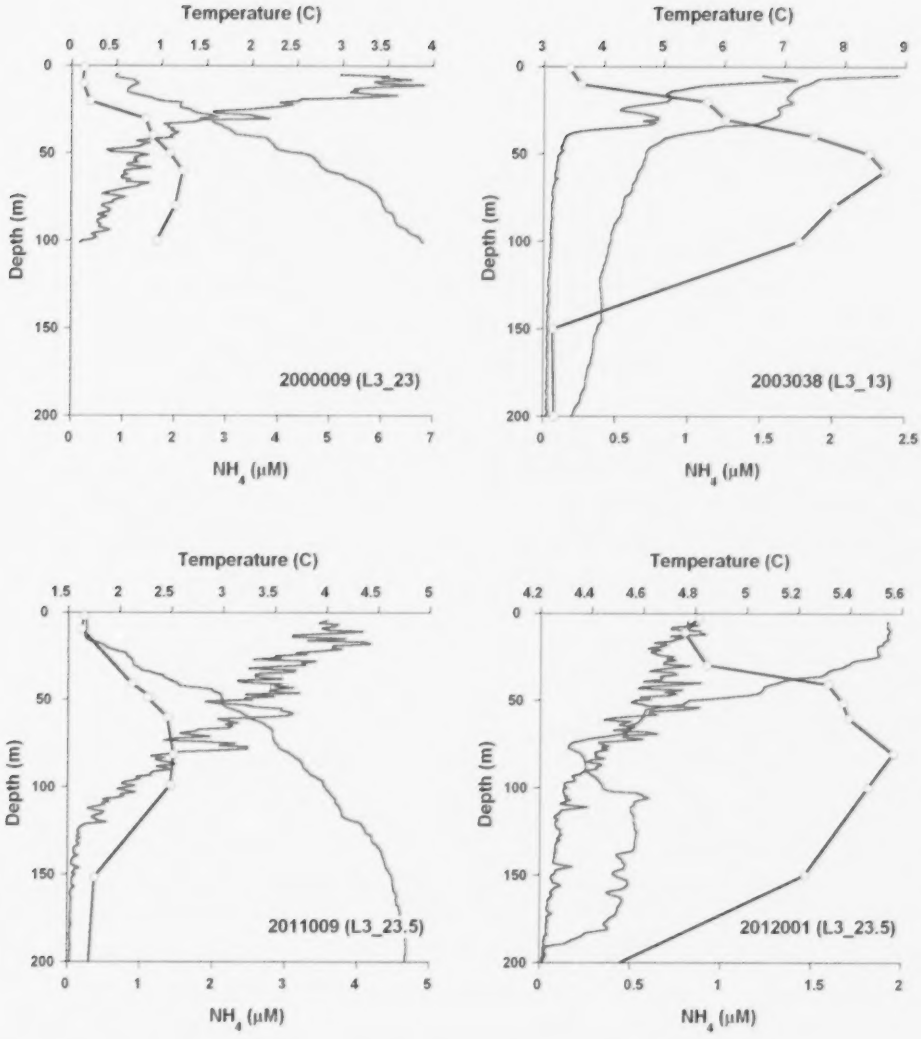

Figure 8: Vertical profiles (upper 200 m) of temperature (^{o}C, red), chlorophyll fluorescence (rel units, green) and NH_4 (μM, blue), Central Labrador Basin: broad subsurface NH_4 maximum.

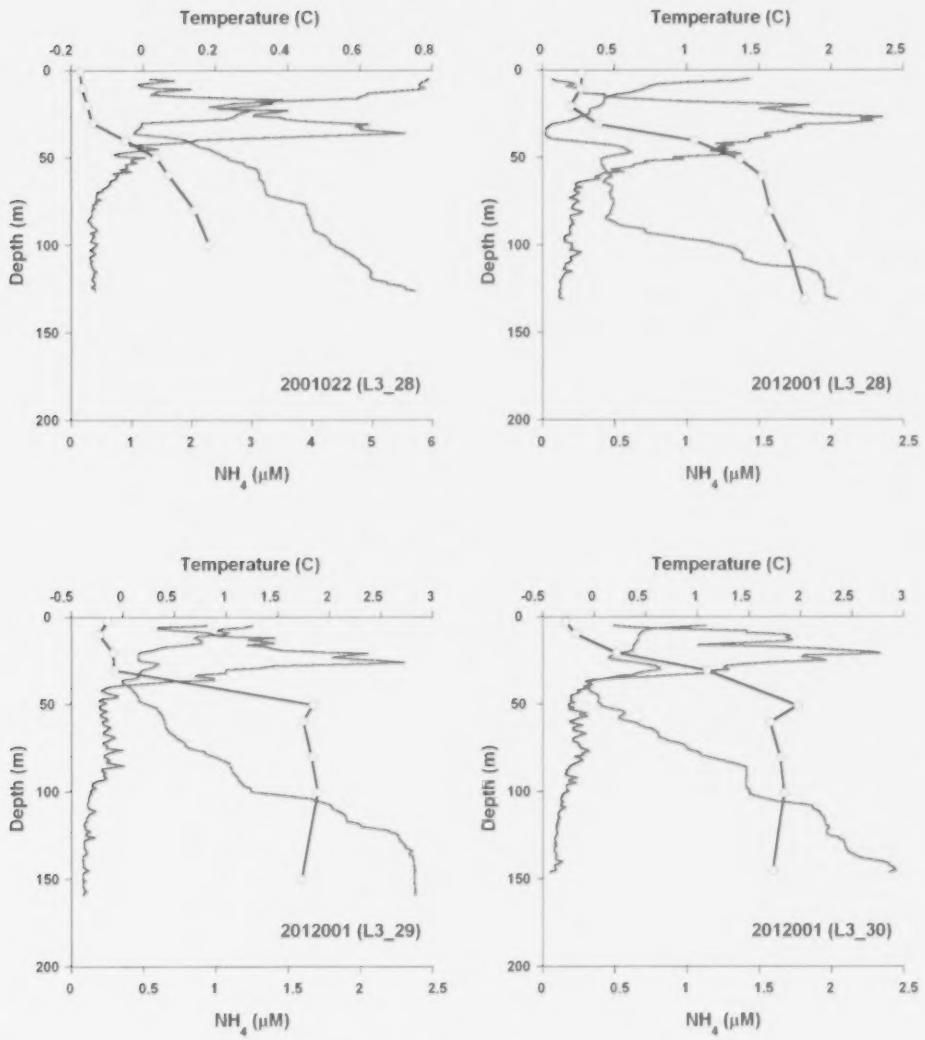

Figure 9: Vertical profiles (upper 200 m) of temperature (^{o}C, red), chlorophyll fluorescence (rel units, green) and NH_4 (µM, blue), Greenland Shelf: subsurface NH_4 maximum.

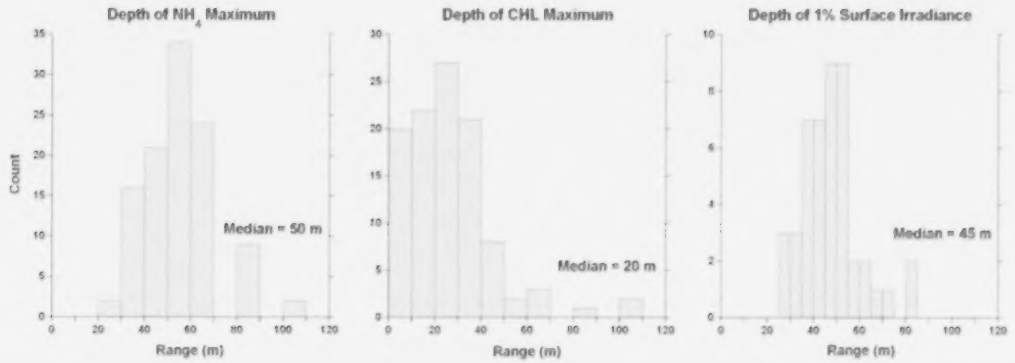

Figure 10: Depth of subsurface NH_4 maxima compared with chlorophyll *a* maxima and euphotic depth (1% light level), 1999-2004.

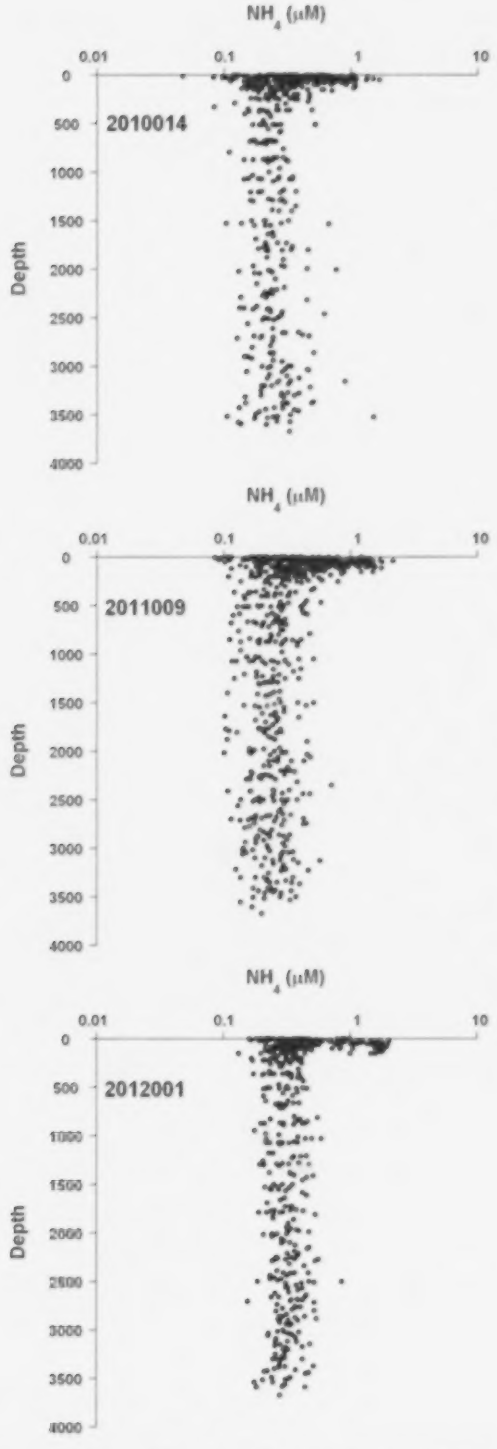

Figure 11: Full-depth vertical profiles of NH_4, all stations along the L3 line, 2010-2012. 90 %tile concentrations (>200 m): 2010 = 0.16-0.37 µM; 2011 = 0.15-0.39 µM; 2012 = 0.23-0.45 µM.

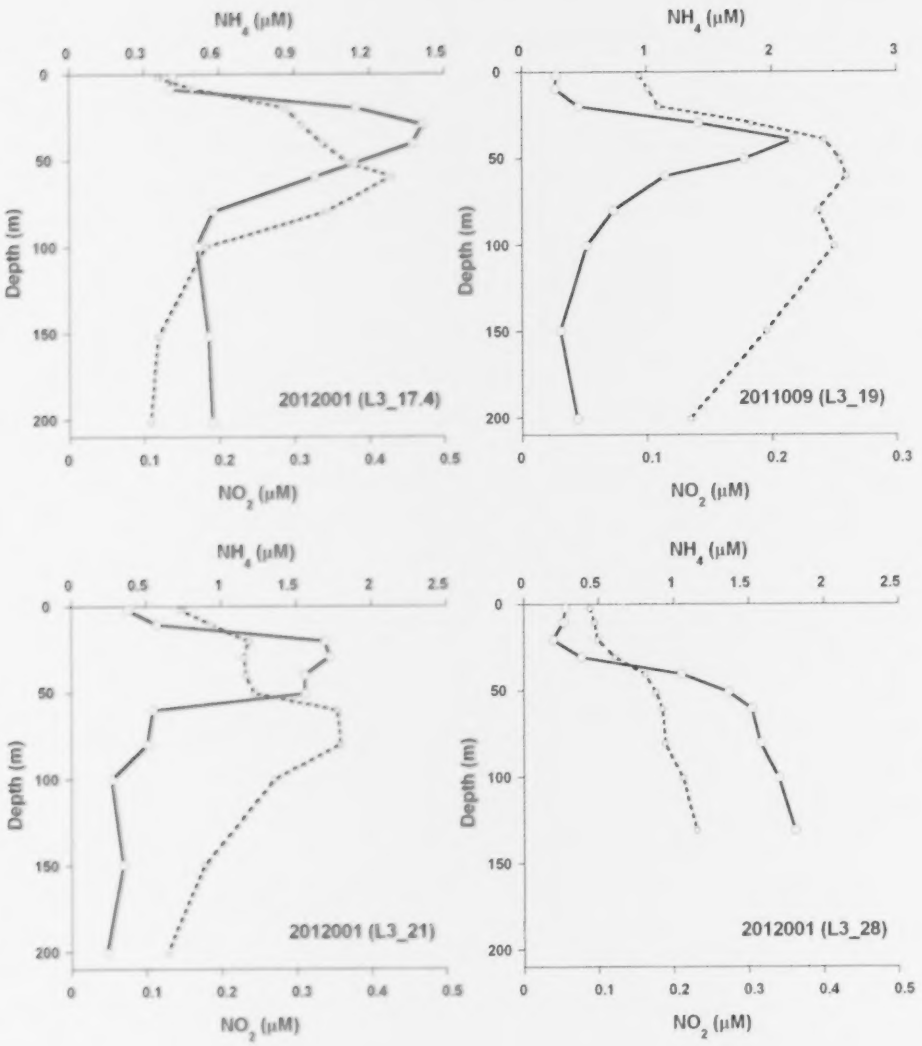

Figure 12: Vertical profiles (upper 200 m) of NH_4 (solid line) and NO_2 (dashed line) at selected stations, µM.

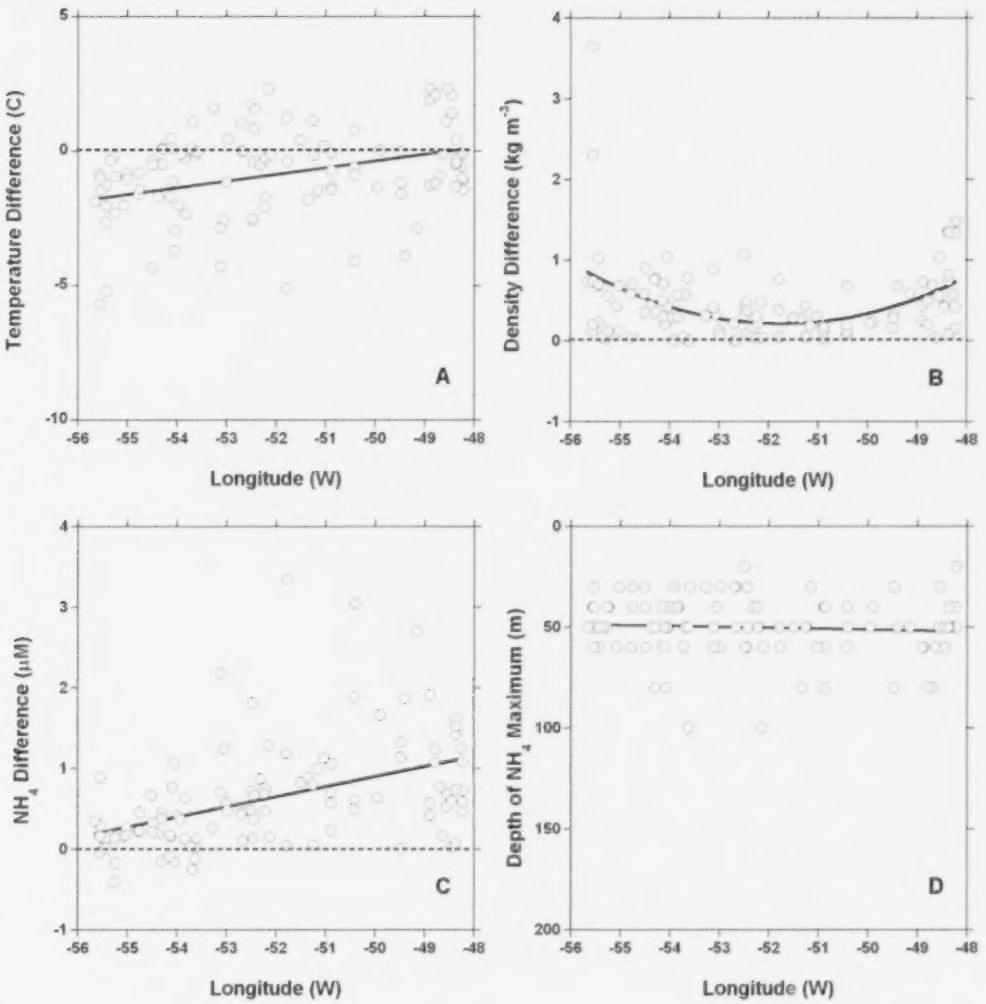

Figure 13: Variability of the vertical structure (difference between surface and depth of NH_4 maximum) of (A) temperature, (B) density, (C) NH_4 and (D) depth of NH_4 maximum along the L3 Line, all years (1999-2012). Lines are least-squares linear (panels A, C, D) or 2nd order polynomial (panel B) fits.

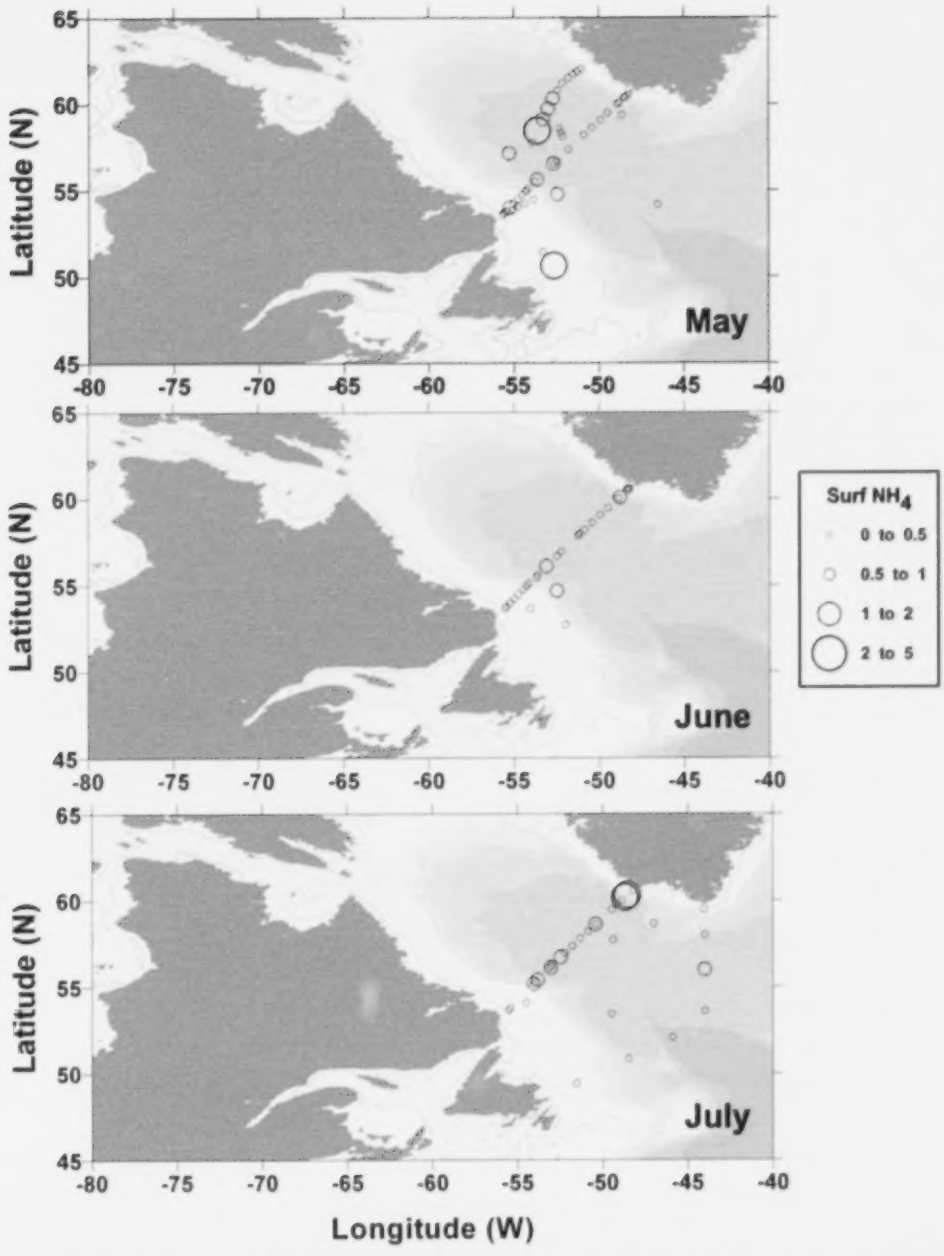

Figure 14: Regional variability in surface NH_4 concentration, by month: May June and July. Median concentrations by month: May = 0.30 μM, June = 0.29 μM, July = 0.26 μM.

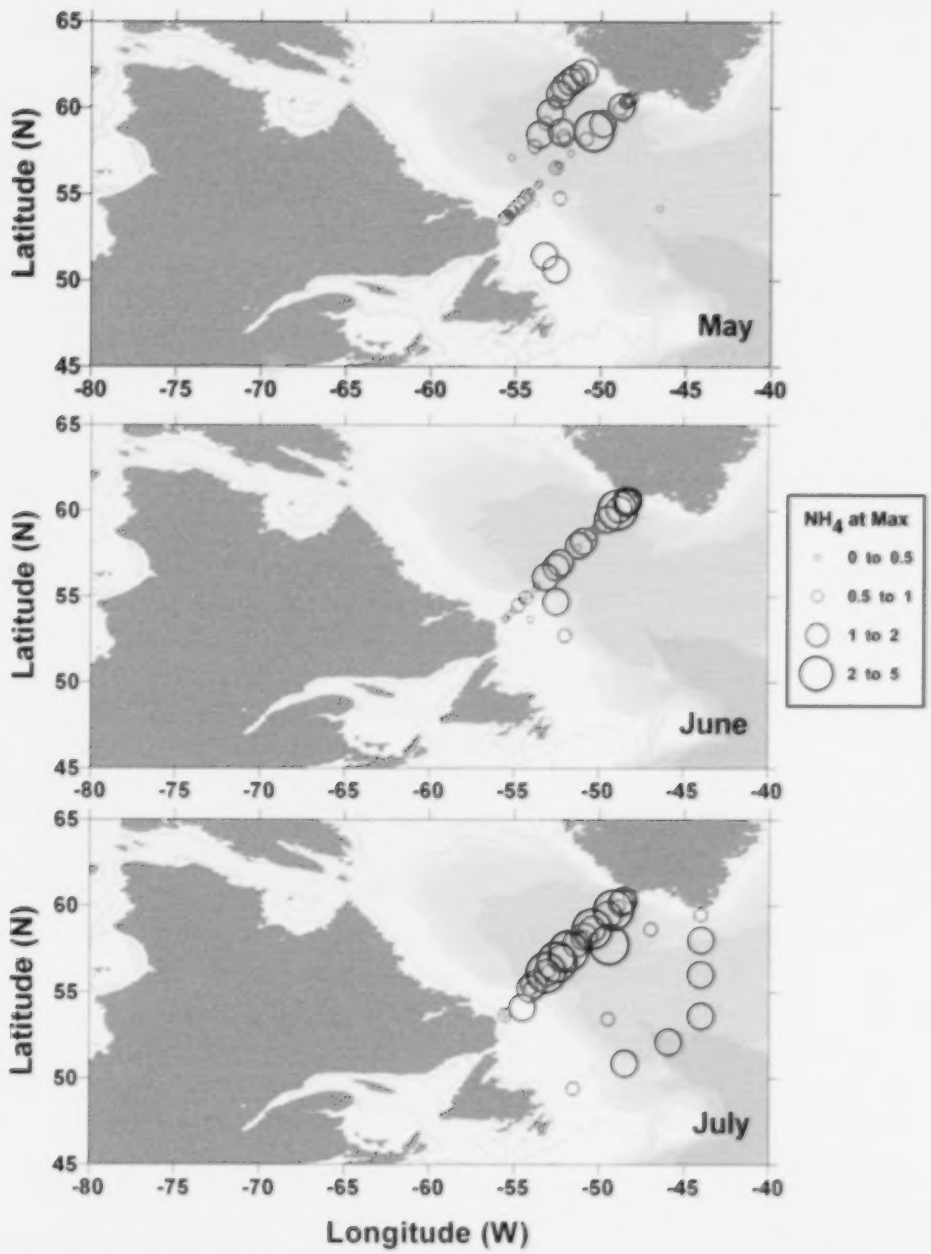

Figure 15: Regional variability in NH_4 concentration at the subsurface maximum, by month: May, June and July. Median concentrations by month: May = 0.63 μM, June = 0.89 μM, July = 1.12 μM.

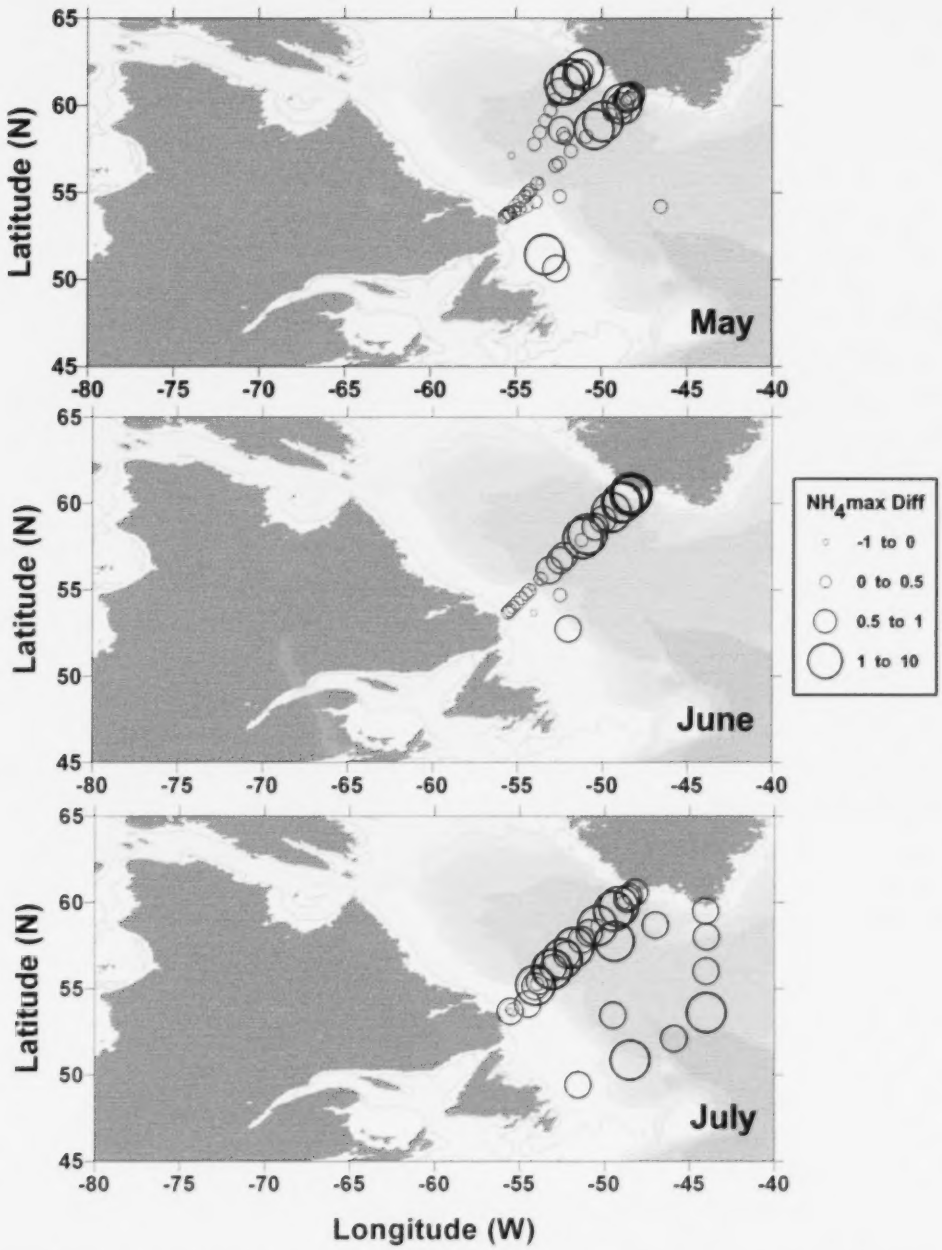

Figure 16: Regional variability in the difference in NH_4 concentrations between surface and subsurface maximum, by month: May, June and July. Median concentrations by month: May = 0.27 μM, June = 0.62 μM, July = 0.75 μM.

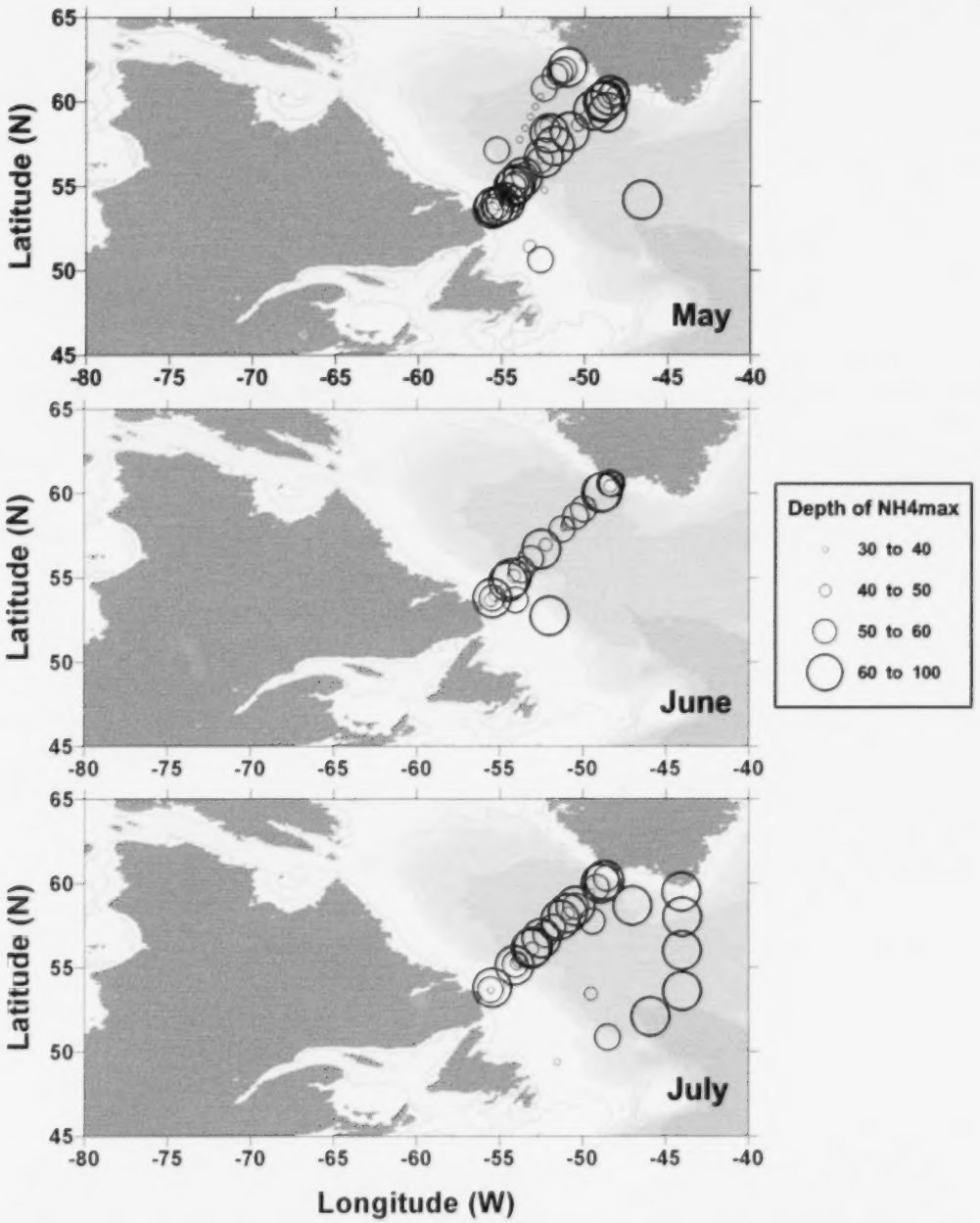

Figure 17: Regional variability in the depth of the subsurface NH_4 maximum, by month: May, June and July. Median depth by month: May = 50 m, June = 50 m, July = 50 m.

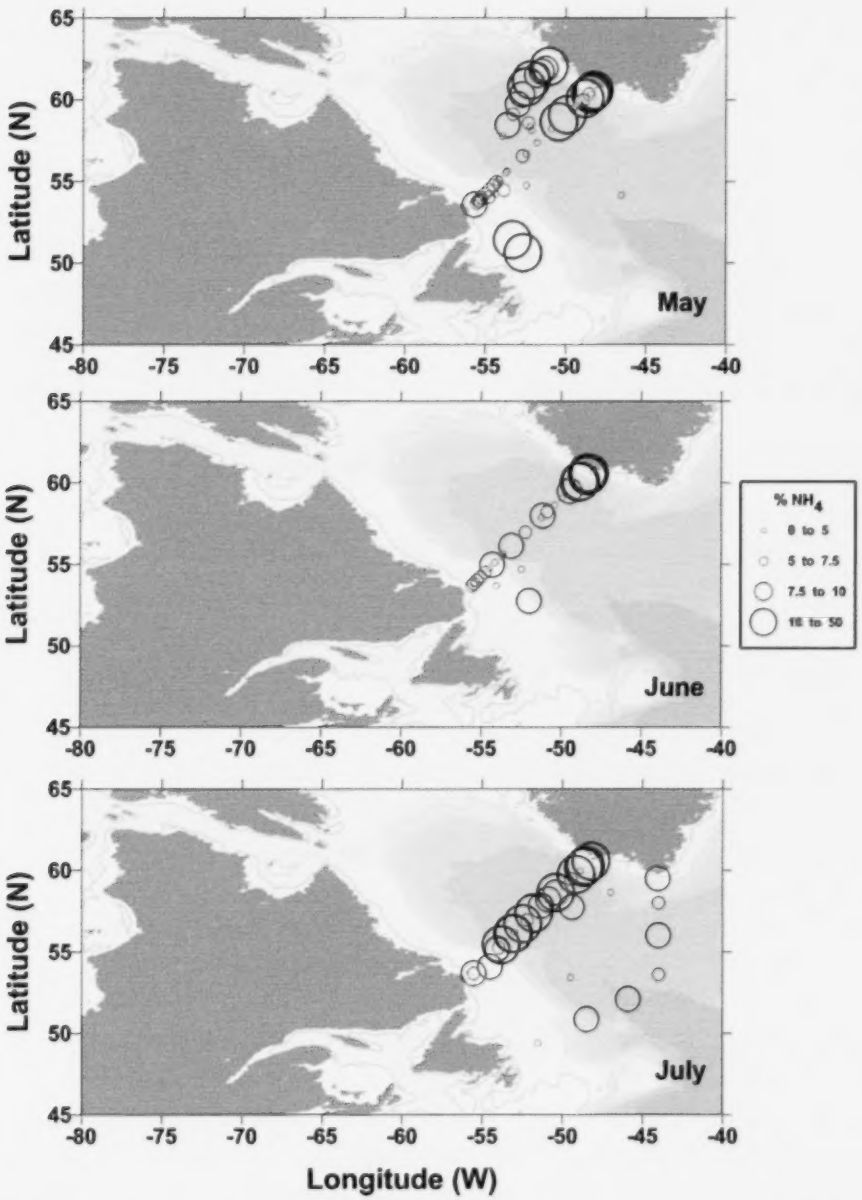

Figure 18: NH_4, as a % of total inorganic-N (NO_3 + NO_2 + NH_4) inventories in the upper 100 m, by month. Median percentage by month: May = 5.9%, June = 6.0%, July = 8.0%.

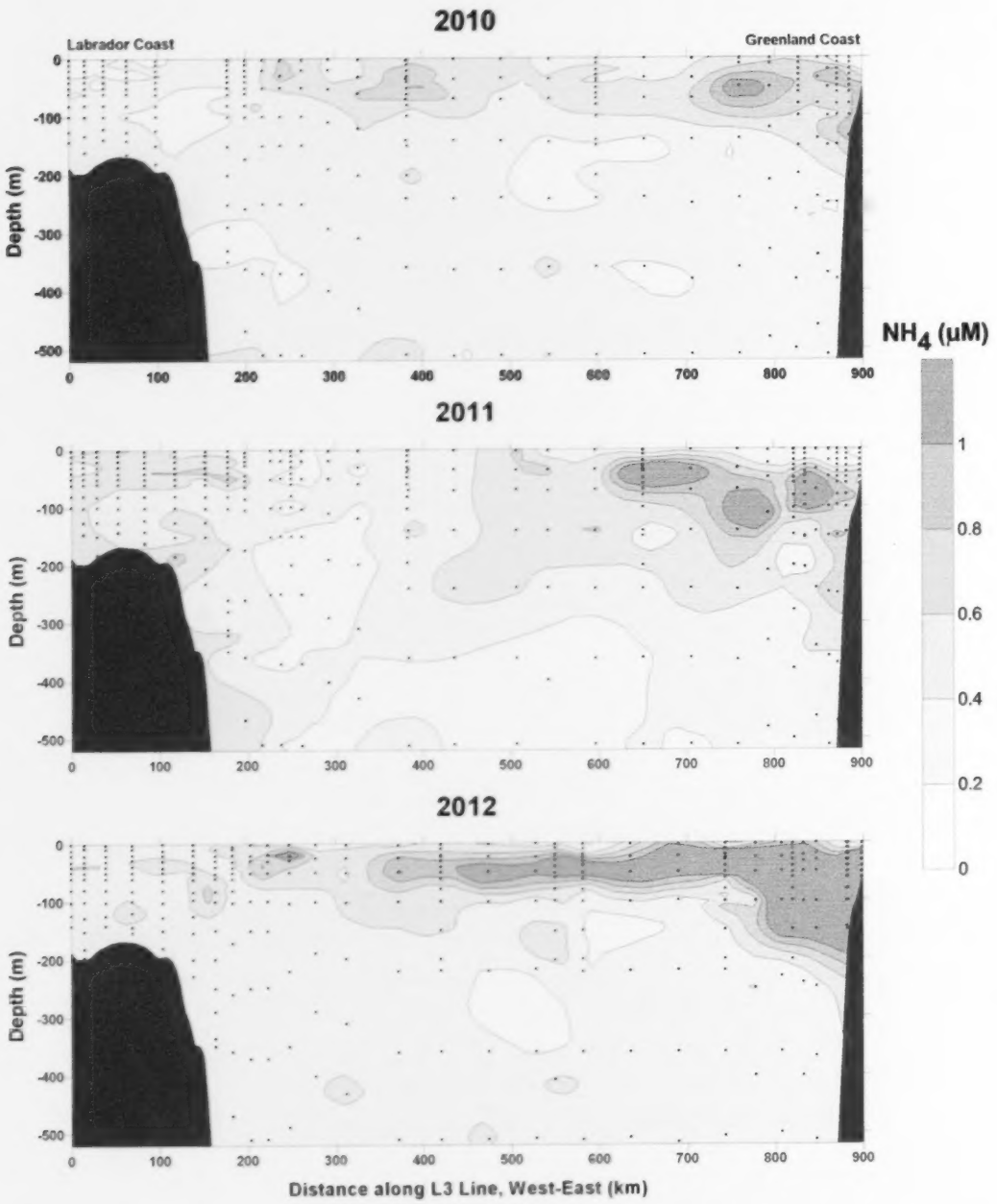

Figure 19: NH_4 concentrations in the upper 500 m along the L3 Line: 2010-2012, μM.

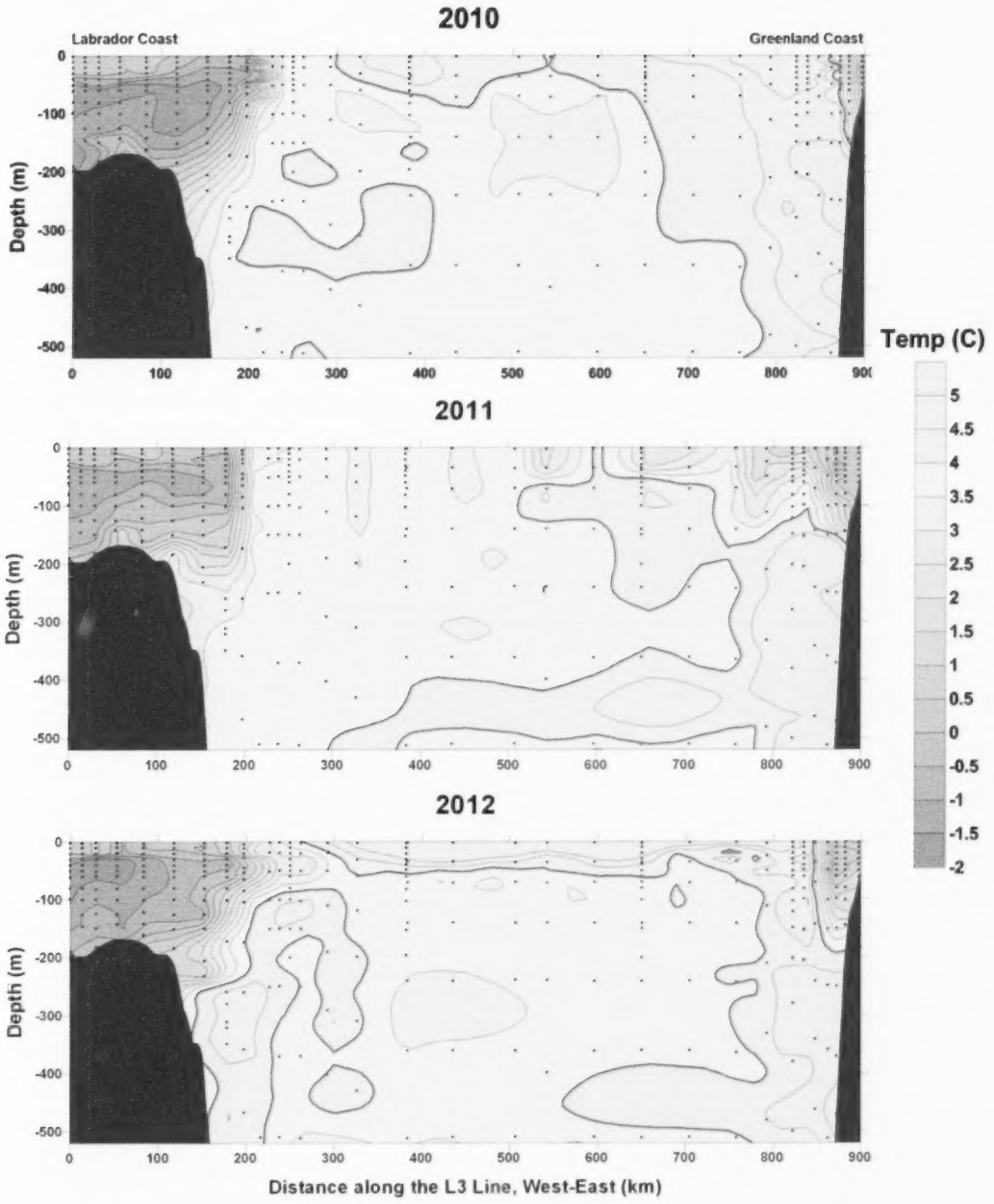

Figure 20: Temperature in the upper 500 m along the L3 Line, 2010- 2012. North Atlantic water (>4 ^{o}C) highlighted.

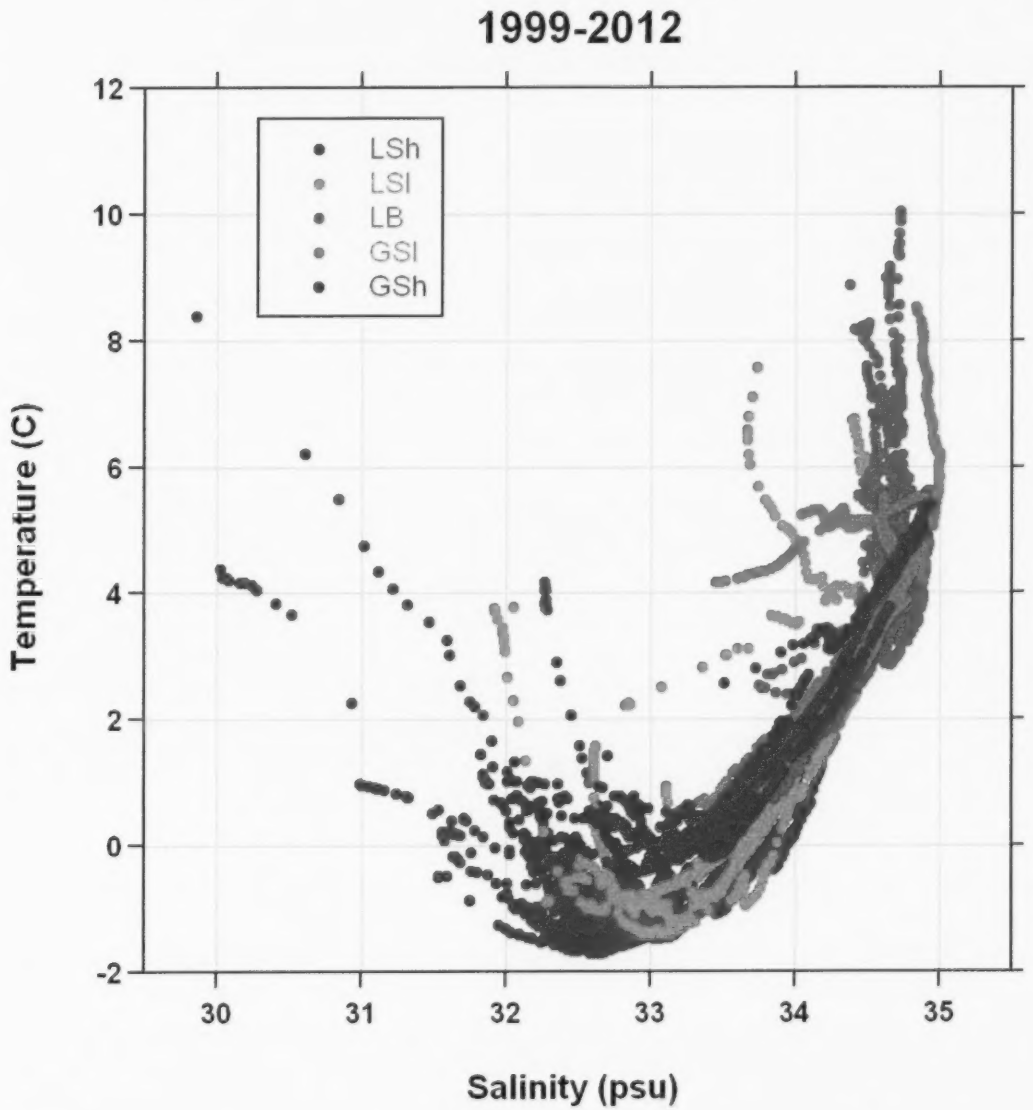

Figure 21: T-S properties along the L3 Line, 1999-2012, colour-coded by region: Labrador Shelf/Slope(LSh, LSl), Central Labrador Basin (LB), Greenland Shelf/Slope (GSh, GSl).

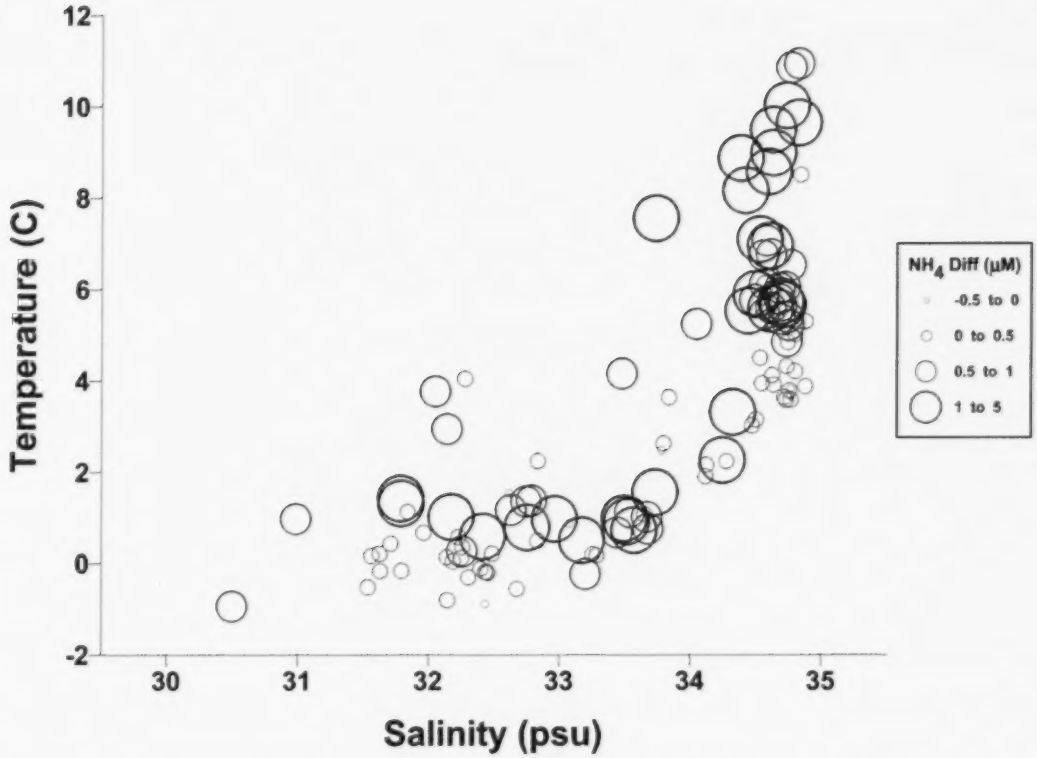

Figure 22: Variability in subsurface NH_4 maxima (µM) relative to T-S properties, 1999-2012.

Figure 23: Satellite ocean colour imagery (SeaWiFS climatology, 1999-2010) showing the time sequence of development of the spring phytoplankton bloom in the Labrador Sea area; the early (late April) bloom off the coast of Greenland and later (late June) bloom in the western Labrador Sea basin are prominent. White space = cloud cover or ice.

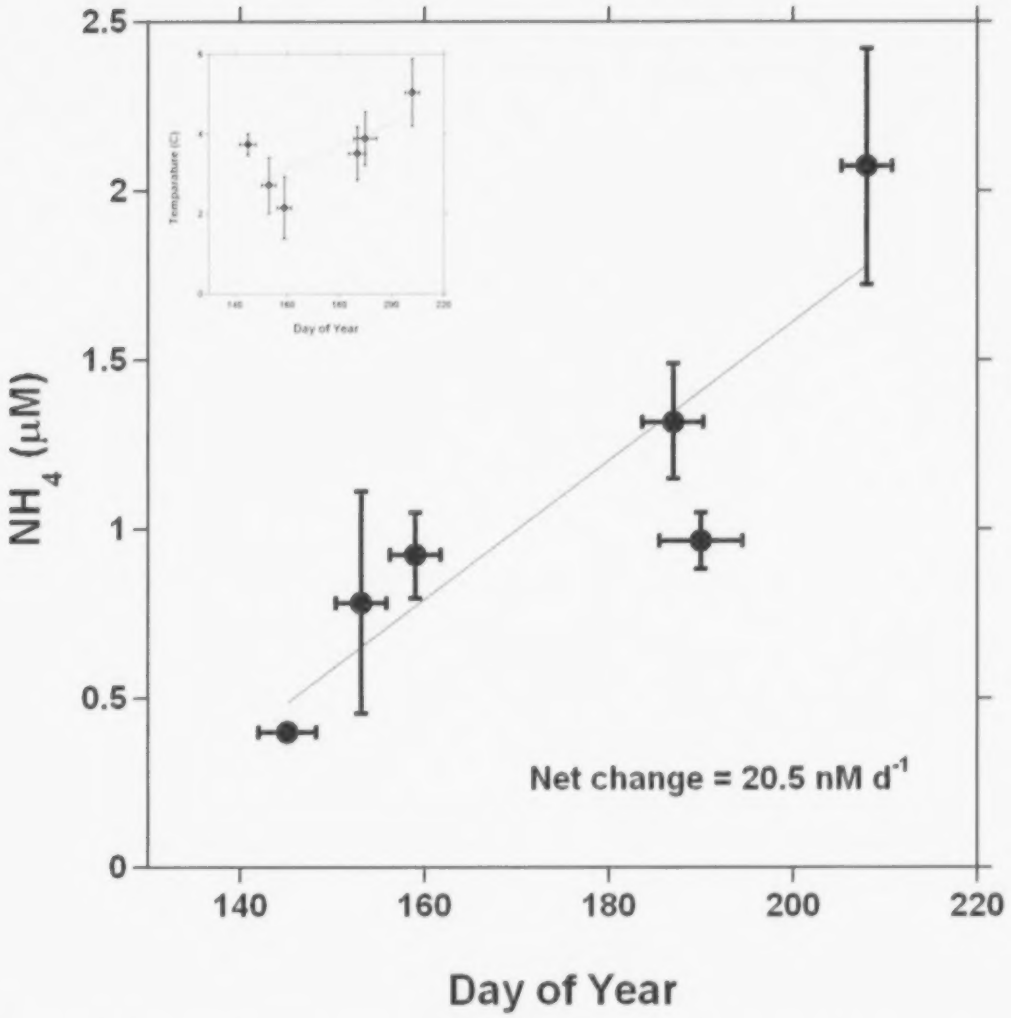

Figure 24: Increase in NH_4 concentration (μM) at the subsurface maximum over time, spring to summer 1999-2004 (inset: temperature change at the subsurface maximum over time). Mission mean values where vertical/horizontal bars are +/- 1 SD. Lines are least-squares linear fits.